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# *OUTLINES OF A NEW SYSTEM OF THERMODYNAMIC CHEMISTRY.*

BY GILBERT NEWTON LEWIS.

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# OUTLINES OF A NEW SYSTEM OF THERMODYNAMIC CHEMISTRY.

By Gilbert Newton Lewis.

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In the rapid development of theoretical chemistry, in which the two laws of energy have played so important a rôle, two thermodynamic methods have been widely used. The first, employed by Gibbs, Duhem, Planck, and others, is based on the fundamental equations of entropy and the thermodynamic potential. The second, employed by such men as van't Hoff, Ostwald, Nernst, and Arrhenius, consists in the direct application to special problems of the so-called cyclic process.

The first method is general and exact, and has been a favorite with mathematicians and physicists, those who were already familiar with the use of the potential theory in mechanics. But unfortunately, except in name there is little analogy between physico-chemical equilibrium and the equilibrium in a mechanical system, and it is perhaps for this reason that the method has failed to commend itself to the majority of chemists. It must be admitted that it is the second method to which we owe nearly all of the advances that have been made during the last thirty years through the application of thermodynamics to chemical problems, and which is now chiefly used by investigators and in the text-books of physical chemistry.

Yet the application of this method has been unsystematic and often inexact, and has produced a large number of disconnected equations, largely of an approximate character. An inspection of any treatise on physical chemistry shows that the majority of the laws and equations obtained by the application of thermodynamics, are qualified by the assumption that some vapor behaves like a perfect gas, or some solu-

tion like a perfect solution.[1] As examples may be cited the mass law, the law of change of solubility with the temperature, the law of the lowering of vapor pressure by a solute, the law of Nernst for the electromotive force of a concentration cell, and many other equally important generalizations.

It is probable that no one of these laws is ever strictly true. As approximations to the truth they have been of the greatest service. But now that their utility has been demonstrated, the attention of a progressive science cannot rest upon their acknowledged triumphs, but must turn to the investigation of their inaccuracies and their limitations. From the study of the deviations from the simple gas laws has grown one of the most interesting chapters of chemistry. So from a study of the deviations from such a law as the mass law we may expect results of the highest value.

In such more exact investigations the old approximate equations of thermodynamic chemistry will no longer suffice. We must either turn to the precise, but rather abstruse, equations of entropy and the thermodynamic potential, or modify the methods which are in more common use, in such a way as to render them exact.

The latter plan is the one followed in the present paper, the aim of which is to develop by familiar methods a systematic set of thermodynamic equations entirely similar in form to those which are now in use, but rigorously exact.

The following development is necessarily brief and concise, but I have hoped, nevertheless, to make it intelligible to any chemist who is familiar with the simpler theorems of elementary calculus.

## The Escaping Tendency.

The meaning of the term "escaping tendency" may be illustrated by an analogy taken from another branch of applied thermodynamics, — the theory of heat.

The conception of temperature owes its utility to the existence of two fundamental laws of heat exchange. When two bodies are brought together and there is no transfer of heat from one to the other, they are said to be at the same temperature; but if such a transfer takes place, the body which loses heat is said to be at a higher temperature than the other. Now the two laws of temperature are the following: (1) Two bodies which have the same temperature as a third, have the

[1] We may speak of a perfect solution as we speak of a perfect gas, that is, one which obeys the laws of an infinitely dilute solution.

same temperature as each other. (2) If a body A has a higher temperature than the body B, it has a higher temperature than any other body of the same temperature as B.

These are not self-evident truths, but empirical laws. If they did not exist, the idea of temperature would lose all value. Temperature determines the distribution of energy in a system, and we may regard the temperature of a body as a measure of the tendency of its internal heat to escape into other bodies.

There are in chemistry two laws which are in every way analogous to the laws of thermal exchange. If a system is composed of several parts, A, B, C, D, containing a given molecular species, X, the two fundamental laws concerning the distribution of X throughout the system are the following: (1) If when the phases A and B are brought together there is no transfer of X from one to the other, and if the same is true of A and C, then when B and C are brought together there will likewise be no transfer of X. (2) If X passes from the phase D to the phase A when they are brought together, then it will also pass from D to B, or to C, or to any phase which is in equilibrium with A as regards the distribution of X. It is obvious that these two laws follow directly from the fundamental laws of thermodynamics, for if they were not true a system could be constructed capable of perpetual motion.

The escaping tendency of a given molecular species in a given state is therefore analogous to temperature, and the two laws of escaping tendency are as follows: If the escaping tendency of a given molecular species, X, is the same in two phases, then X will not of itself pass from one phase to the other. If the escaping tendency of X is greater in one phase, it will pass from this phase into the other, when the two are brought together.

Let us illustrate the meaning of the escaping tendency by an example. When in a pure liquid a small quantity of some other substance is dissolved, the vapor pressure of the liquid is diminished, its freezing point is lowered, its boiling point is raised, its solubility in another solvent is diminished.[2] All these laws are comprised in the simple statement, that the escaping tendency of the solvent is diminished by the addition of the solute.

The idea of temperature was understood long before any suitable measure of temperature was found. Then the mercury thermometer was invented, later the gas thermometer, and finally in the absolute

[2] So also the tendency of the liquid to take part in any chemical reaction is diminished, but until a later section of this paper our discussion will be limited to processes in which a given molecular species passes from one phase to another without any other change.

thermodynamic scale we possess the ideal measure of temperature. So indeed the idea of escaping tendency, although not distinctly formulated, has been tacitly recognized and used, and as a measure of the escaping tendency the vapor pressure has been employed. Now if all vapors obeyed the laws of a perfect gas, probably no better measure could be found. But this is never strictly the case, and the more the vapor departs from the ideal condition the more unsatisfactory is the vapor pressure as a measure of escaping tendency. By introducing a more satisfactory measure of escaping tendency we may gain advantages similar to those which resulted from the substitution of the absolute scale of temperature for the mercury scale.

Such a measure of the escaping tendency I have described and used in a previous paper.[3] It was called the fugacity, and so defined that the fugacity of a perfect gas is equal to its pressure. The fugacity of an imperfect gas differs, however, from the gas pressure by an amount which is greater, the more the gas deviates from the gas law.

The idea of fugacity is thus evolved from the use of vapor pressure as a measure of escaping tendency. When a substance is in equilibrium with its vapor, the fugacity, in order to fulfil the laws of escaping tendency, must be the same in both. The fugacity of a substance is therefore equal to its vapor pressure if the vapor behaves like a perfect gas. Speaking in terms not very precise, we may say that *the fugacity of a substance is equal to the vapor pressure that the substance would have if its vapor were a perfect gas.* It has been shown in the preceding paper that for a given substance in a given state the fugacity is a definite property of which the numerical value can in most cases be readily determined, and which is well suited to serve as an exact measure of the escaping tendency.

In many thermodynamic equations it is convenient to use concentrations instead of pressures. Likewise we shall find it desirable to introduce besides the fugacity, which has the dimensions of pressure, another quantity which has the dimensions of concentration. This quantity we will call the *activity*, and denote by the symbol $\xi$. The activity will be defined in terms of the fugacity, $\psi$, by the following equation,

$$\xi = \frac{\psi}{RT}, \qquad \text{I}$$

where $R$ is the gas constant and $T$ is the absolute temperature. Since the fugacity of a perfect gas is equal to its pressure, it is obvious that

[3] The Law of Physico-Chemical Change. Zeit. phys. Chem., **38**, 205 (1901); These Proceedings, **37**, 49 (1901).

the activity of a perfect gas is equal to its concentration. If $R$ has its ordinary value, $\xi$ will be given in mols per liter.

Both the fugacity and the activity are well adapted to serve as measures of the escaping tendency. Indeed, for isothermal changes the equations in which the two quantities enter are as a rule identical. However, since the equations for the change of fugacity with the temperature are a little less simple than those of the activity, we shall choose the latter quantity for our present purpose. We shall start with a simple definition of the activity, and proceed to show that the change of the activity with the variables which determine the state of the system may be expressed by a series of exact equations which are of the same form as many of the familiar approximate equations for vapor pressure, solubility, etc.

On account of the large scope of this undertaking our consideration will be limited to those systems which are completely determined by the temperature, the pressure, and the composition of the various phases. How the work may be extended to include other variables, such as surface tension, has been indicated in the preceding paper.

## Fundamental Laws and Assumptions.

The following work will be based on the two laws of thermodynamics and upon the law that every gas and every solution as the concentration diminishes approaches as a limit the perfect gas and the perfect solution. Besides these we shall use the following definitions of the activity.

When the activity of a substance is the same in two phases, that substance will not of itself pass from one phase to the other.

When the activity of a substance is greater in one phase than in another, the substance will pass from the one phase to the other, when they are brought together.

The activity of a perfect gas is equal to its concentration.

The activity of the solute in a perfect solution, at constant temperature and pressure, is proportional to its concentration.

We shall see that these statements suffice to define the activity of a substance in any state, and except in unusual cases enable us to calculate its numerical value.

No further assumptions are necessary, but *since our aim will be to lay stress rather on the exactness of the results obtained than upon the mathematical rigor of the method by which they are demonstrated*, we shall adopt as working aids the following assumptions:

(1) For every molecular species we will assume that an *ideal solvent*

may be found (or imagined) in which that species dissolves to form a perfect solution, at all concentrations up to that of the saturated solution.

(2) We may further assume that the ideal solvent chosen is one which suffers neither increase nor decrease of volume when the substance in question is dissolved at constant temperature and pressure. In other words, the volume of the ideal solution is the same as that of the ideal solvent it contains.[4]

(3) In dealing with mixtures, use will be made of any kind of semipermeable membrane, real or imaginable, that may prove serviceable.

Probably in no case can the ideal solvent or the perfect semipermeable membrane be actually found. They will be employed as convenient fictions for the purpose of obtaining results which could be obtained without their aid, but by less simple methods.

## Equations of a Solution in the Ideal Solvent.

Let us consider the vapor of a substance X, together with a solution of X in an ideal solvent. From the laws stated in the preceding section it may readily be shown that as the quantity of X is diminished, and the solution and the vapor become less concentrated, the ratio between the concentrations of X in the two phases approaches a constant value.[5] In other words, if $c$ represents the concentration of X in the solution, $c'$ in the vapor, then at infinite dilution,

$$c' = \rho c,$$

where $\rho$ is a constant, when the temperature and pressure are constant, and may be called the distribution coefficient between solution and vapor at infinite dilution. This equation is merely the exact statement of Henry's law.

Since the two phases are kept in equilibrium, the activity of X must always be the same in one phase as in the other, that is,

$$\xi = \xi'.$$

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[4] This assumption is of minor consequence, and is introduced merely to simplify some of the mathematical work. It can be omitted without materially changing the following work.

[5] Since our purpose is to develop a set of exact equations, but not to place too much emphasis upon the formal rigor with which those equations are obtained, it will not be necessary to repeat the proof of propositions which have already been proved elsewhere and which can obviously be obtained by familiar methods.

At infinite dilution the vapor of X becomes a perfect gas, and by definition

$$\xi' = c'.$$

Hence at infinite dilution

$$\xi = c' = \rho c.$$

$\xi$ is the activity of X in the ideal solvent, and $c$ is its concentration, and by definition $\xi$ is proportional to $c$ for all concentrations which we shall consider. Hence, not merely at infinite dilution but in general one of the fundamental equations of the ideal solution is,

$$\xi = \rho c. \qquad \text{II}^*$$ [6]

From this another useful equation may be obtained. In the case of the ideal solution we have for the osmotic pressure, $\Pi$, the equation,

$$\Pi = cRT.$$

Hence

$$\xi = \frac{\rho \Pi}{RT}. \qquad \text{III}^*$$

The quantity $\rho$ varies with the temperature. In order to find the law of this variation we may once more consider the equilibrium at infinite dilution between the vapor of X and the solution of X in the ideal solvent.

Since we are dealing here with the ideal solution and with a perfect gas, the following special form of the equation of van't Hoff can be proved by familiar methods to be entirely exact.

$$\frac{d \ln \rho}{dT} = \frac{U_{(\text{IV})}}{RT^2}, \qquad \text{IV}$$

where ln signifies natural logarithm, and $U_{(\text{IV})}$[7] is the increase of internal energy when one mol of X passes from the ideal solvent into the infinitely attenuated vapor.

With the aid of these equations we are now prepared to undertake a systematic study of the laws of physico-chemical change. It is to be noted that *from each one of the following exact equations two important approximate equations may be obtained directly*, — one for solubility,

[6] Numbered equations, such as those of the ideal solution, which are only true under special conditions, will be marked with the asterisk.

[7] Since it will be necessary to use the symbol $U$ for various kinds of internal energy change, a particular value of $U$ will be designated by the number of the equation in which it first appears.

by substituting for the activity the concentration of a saturated solution, and one for vapor pressure, by substituting for the activity the concentration of the saturated vapor.

## The Influence of Pressure and Temperature upon the Activity of a Simple Substance.

Let us consider a pure substance in any state, — solid, liquid, or gaseous, — and find the effect upon its activity : first, of a change of pressure at constant temperature, and second, of a change of temperature at constant pressure. Since the equations we are about to obtain are special cases of equations IX and XII, of which a complete proof is given in a later section, a less thorough derivation will here suffice.

In the preceding paper a formula was obtained (equation 14) for the influence of pressure on the fugacity of a pure substance, namely,

$$\left(\frac{\partial \ln \psi}{\partial P}\right)_T = \frac{v}{RT},$$

where $\psi$ is the fugacity and $v$ the molecular volume. Combining this equation with equation I of the present paper, we find, since $RT$ is constant,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_T = \frac{v}{RT}. \qquad \text{V}$$

This is a perfectly general equation for the influence of pressure upon the activity of a pure substance. Since the second member of this equation is always a positive quantity, it is obvious that an increase of pressure always causes an increase in the activity.

In order to determine the influence of temperature, let us consider a substance X, in contact with its saturated solution in an ideal solvent. The solubility as measured by the osmotic pressure, $\Pi$, varies with the temperature according to the well-known equation

$$\left(\frac{\partial \ln \Pi}{\partial T}\right)_P = \frac{Q}{RT^2}, \qquad \text{VI*}$$

which, since we are dealing with the ideal solution, can be shown to be entirely exact. $Q$ is the total heat absorbed when one mol of X dissolves reversibly in the ideal solvent. It is obviously the sum of three terms, — the increase in internal energy, the osmotic work done, and the work done against the external pressure, $P$. (According to one of our fundamental assumptions the volume of the ideal solvent does not

change when X dissolves.) The first of these terms we will call $U_{(VII)}$; the second, according to the principle of van't Hoff, is equal to $RT$; and the third is equal to $-Pv$, where $v$ is the molecular volume of pure X. We may write equation VI, therefore, in the form

$$\left(\frac{\partial \ln \Pi}{\partial T}\right)_P = \frac{U_{(VII)} + RT - Pv}{RT^2}. \qquad \text{VII*}$$

Now the activity, $\xi$, of X in the pure state is always equal to that in the saturated solution. The latter is related to $\Pi$, according to equation III, by the formula,

$$\Pi = \frac{\xi RT}{\rho}.$$

Substituting this value of $\Pi$ in equation VII gives,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_P - \left(\frac{\partial \ln \rho}{\partial T}\right)_P + \frac{1}{T} = \frac{U_{(VII)} + RT - Pv}{RT^2}.$$

Substituting for the second term the value given by equation IV, and simplifying, we have,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_P = \frac{U_{(VII)} + U_{(IV)} - Pv}{RT^2}.$$

$U_{(VII)}$ is the increase in internal energy when a mol of X dissolves in the ideal solvent and $U_{(IV)}$ is the increase when it passes from that solution into the state of infinitely attenuated vapor. The sum of these two is the increase in internal energy when a mol of X is evaporated and the vapor expanded indefinitely, or in other words it is the increase in internal energy when a mol of X evaporates into a vacuum. This important quantity, which we may call for the sake of brevity the *ideal heat of evaporation*, will be designated by the symbol $\Upsilon$. Substituting it in the last equation gives,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_P = \frac{\Upsilon - Pv}{RT^2}. \qquad \text{VIII}$$

This is the general equation for the effect of temperature on the activity of any pure solid, liquid, or gas. Except in very rare cases the second member is positive and $\xi$ increases with $T$.

## Applications of the Preceding Equations.

A few examples will serve to illustrate the mode of application of equations V and VIII.

Two phases of the same substance, ice and water, for example, are in equilibrium at a given temperature and pressure. If the pressure on either phase alone is increased, the activity in that phase is increased, and the phase must disappear. If the pressure upon both phases is increased by the same amount, the activity is increased more in the phase of largest molecular volume, namely the ice, and it will disappear. By increasing the pressure on the ice by the amount $dP$, and that on the water by a greater amount, $dP'$, it is possible to maintain equilibrium. Let us see what relation these two increments of pressure must bear to each other. Let $\xi$, $P$, $v$, and $\xi'$, $P'$, $v'$, represent the activity, pressure, and molecular volume of the ice and the water, respectively. From equation V,

$$d \ln \xi = \frac{v}{RT} dP, \quad \text{and} \quad d \ln \xi' = \frac{v'}{RT} dP'.$$

In order to maintain equilibrium we must always keep $\xi$ equal to $\xi'$. Hence,

$$d\xi = d\xi', \quad \text{or} \quad d \ln \xi = d \ln \xi'.$$

Therefore the condition of continued equilibrium is,

$$\frac{v}{RT} dP = \frac{v'}{RT} dP' \quad \text{and} \quad \frac{dP}{dP'} = \frac{v'}{v}.$$

In order to maintain equilibrium the increments of pressure on the two phases must be inversely proportional to the molecular volumes.[8]

As a second illustration let us consider the same system of ice and water subject to a simultaneous change of pressure and temperature. The effect of increasing the pressure equally on both phases is to increase the activity of the ice more than that of the water. An increase of temperature has the same effect. By increasing the pressure and at the same time lowering the temperature, equilibrium may be maintained. The condition of equilibrium, as in the preceding case, is,

$$d \ln \xi = d \ln \xi',$$

but in this case the change in $\xi$ and in $\xi'$ is due in part to change in temperature, in part to change in pressure, that is,

[8] For a proof of this equation by other methods, see Lewis, Z. physik. Chem., **35**, 343 (1900); These Proceedings, **36**, 145 (1900).

$$d \ln \xi = \left(\frac{\partial \ln \xi}{\partial T}\right)_P dT + \left(\frac{\partial \ln \xi}{\partial P}\right)_T dP,$$

and

$$d \ln \xi' = \left(\frac{\partial \ln \xi'}{\partial T}\right)_P dT + \left(\frac{\partial \ln \xi'}{\partial P}\right)_T dP.$$

Equating the second members of these equations and substituting for the partial differential coefficient their values from equations V and VIII,

$$\frac{\Upsilon - Pv}{RT^2} dT + \frac{v}{RT} dP = \frac{\Upsilon' - Pv'}{RT^2} dT + \frac{v'}{RT} dP,$$

or

$$\frac{\Upsilon - Pv - \Upsilon' + Pv'}{RT^2} dT = \frac{v' - v}{RT} dP.$$

The numerator of the first fraction is obviously equal to the heat of fusion of one mol of ice. Calling this $Q$, we have

$$\frac{dT}{dP} = \frac{(v' - v)\,T}{Q},$$

which is the familiar equation of Thomson for the change of freezing point with the pressure.

As a third illustration of the application of these equations we will consider a general method for determining the numerical value of the activity of a substance. Let us first consider a gas which is at such a pressure as no longer to obey the gas law. According to equation V we may write, for the influence of pressure on the activity, at constant temperature,

$$d \ln \xi = \frac{v}{RT} dP.$$

From this equation we may find the activity at one pressure when it is known at any other, if we know the molecular volume, $v$, as a function of the pressure, $P$. For this purpose we may use any empirical equation, such as that of van der Waals, namely,

$$P = \frac{RT}{v - b} - \frac{a}{v^2}.$$

Differentiating this equation, substituting the value of $dP$ in the preceding equation, and integrating between $v$ and $v'$, we obtain the equation,

$$\ln[\xi(v-b)] - \ln[\xi'(v'-b)] = \frac{b}{v-b} - \frac{b}{v'-b} - \frac{2a}{RTv} + \frac{2a}{RTv'}.$$

From this equation, assuming that the van der Waals formula is true and that the constants $a$ and $b$ are known for a given substance, the activity of that substance can be found at the volume $v$ when it is known at any other volume, $v'$. At infinite volume the activity of the gas, by definition, is equal to its concentration, which is the reciprocal of its molecular volume. It is evident, therefore, that if in the above equation $v'$ approaches infinity, $\xi'$ approaches $\frac{1}{v'}$ or $\frac{1}{v'-b}$, and the second, fourth, and sixth terms in the equation approach zero. Omitting these terms, therefore, and rearranging slightly, we have,

$$\ln \xi = \frac{b}{v-b} - \frac{2a}{RTv} - \ln(v-b).$$

From this equation $\xi$ can be found for any gas at any volume, $v$, provided the formula of van der Waals holds, and the values of $a$ and $b$ are known. Similarly any other empirical equation of condition may be used.

According to Amagat's experiments upon carbon dioxide at 60° the molecular volumes of this gas at 50, 100, 200, and 300 atmospheres, are, respectively, 0.439, 0.147, 0.0605, and 0.0527 liters. From these data I have calculated the values of $a$ and $b$ at this temperature and found,

$$a = 3.1; \quad b = 0.034$$

(pressure being expressed in atmospheres, volume in liters, and R consequently having the value 0.0820).

Substituting these values in the above equations, we obtain the values for the activity of carbon dioxide at 60° given in the following table:

| $P$. | $c$. | $\xi$. | $\xi/c$. |
|---|---|---|---|
| 50 | 2.3 | 1.6 | 0.70 |
| 100 | 6.8 | 2.6 | 0.38 |
| 200 | 16.5 | 3.2 | 0.19 |
| 300 | 19.0 | 4.2 | 0 22 |

The first column gives the pressure, the second gives the concentration in mols per liter $\left(\frac{1}{v}\right)$, the third gives the activity, also in mols per liter, and the fourth gives the ratio of activity to concentration, which for a perfect gas is always unity. The increase in this quotient between 200 and 300 atmospheres is interesting, and the whole table shows how little either the pressure or the concentration of a compressed gas is suited to act as a measure of the escaping tendency.

If instead of determining the activity of gaseous carbon dioxide we desired to determine that of $CO_2$ in some other phase, for example in a solution of sodium bicarbonate in water at a given temperature and concentration, it would be only necessary to know the pressure or the concentration of carbon dioxide gas in equilibrium with that phase. For the activity there would be the same as in the gas, and the latter could be determined by the above method.

This, therefore, is a perfectly general method for determining the numerical value of the activity. However, it is to be emphasized that *in most cases where the conception of activity is useful, it is not necessary to know the numerical value, but only the ratio of the activities in two given states.* This will be illustrated in another section.

## Influence of Pressure, Temperature, and Concentration upon the Activity of the Constituents of a Binary Mixture.

The equations in this section will apply not only to a homogeneous liquid mixture, but also to a gaseous mixture, or solid solution, in fact to any homogeneous phase whatever which is composed of the two molecular species, $X_1$ and $X_2$. The composition of a binary mixture we shall express, following Ostwald, by the molecular fractions (Molenbruche), $N_1$ and $N_2$, so defined that $N_1 + N_2 = 1$. By *one mol of the mixture* we shall mean that amount which contains $N_1$ mols of $X_1$ and $N_2$ of $X_2$. Later, in dealing with mixtures of more than two constituents, the fractions $N_1$, $N_2$, $N_3$, etc., will be similarly defined, so that $N_1 + N_2 + N_3 + \ldots = 1$.

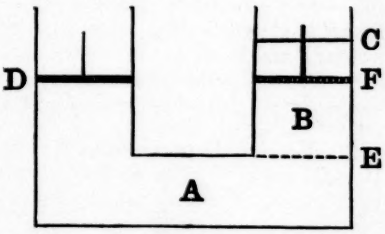


Figure 1.

The influence of pressure upon the activity of either constituent of

a binary mixture may be found by means of the apparatus shown in Figure 1. A contains the mixture of $X_1$ and $X_2$. D is a piston which determines the pressure on A. E is a membrane permeable only to $X_1$. B contains a solution of $X_1$ in its ideal solvent. F is a piston permeable only to the latter. Above F is the pure solvent.

The pressure on the piston F is the osmotic pressure, $\Pi$, of the ideal solution in B. In general if the pressure, $P$, on D is changed, the equilibrium will be disturbed and the substance $X_1$ will pass through E, unless at the same time the pressure on F is changed by a suitable amount. Let us find the mathematical expression for the change in $\Pi$, which just compensates a given change in $P$.

Starting with the piston F at E and with a large (better, an infinite) amount of the mixture in A, occupying the volume V, let us perform isothermally the following cycle of reversible operations.

(1) Keeping the pressure $P$ constant on the piston D, and keeping the pressure on F also constant and equal to the corresponding osmotic pressure, $\Pi$, raise F until one mol of $X_1$ passes into B, where it occupies the volume $v'$. The diminution in the volume of A we will denote by the symbol $\bar{v}$. The work done by the system by means of the pistons F and D is, therefore,

$$A_1 = \Pi v' - P\bar{v}.$$

(2) Now increase the pressure on the piston D to $P + dP$, and at the same time increase the pressure on F to $\Pi + d\Pi$, $d\Pi$ being the increment in $\Pi$ which is necessary to prevent $X_1$ from passing in either direction through E. The volume of A will change from $V - \bar{v}$ to $(V - dV) - (\bar{v} - d\bar{v})$, and the volume of the solution will change from $v'$ to $v' - dv'$. The work done by the system by means of the pistons F and D is,

$$A_2 = -\Pi dv' - P(dV - d\bar{v}).$$

(3) Keeping the pressures on the two pistons constant and equal to $\Pi + d\Pi$ and $P + dP$ respectively, lower F to E, forcing the mol of $X_1$ back into A. The work done by the two pistons is

$$A_3 = -(\Pi + d\Pi)(v' - dv') + (P + dP)(\bar{v} - d\bar{v}).$$

(4) Change the pressure in A back to P. The piston F is stationary, and the work done by the piston D is,

$$A_4 = PdV.$$

The surface C does not change its position during these operations (according to the definition of the ideal solvent). The total work done by the system is therefore equal to the sum of $A_1$, $A_2$, $A_3$, and $A_4$, and since the cycle is isothermal and reversible this sum is equal to zero, by the second law of thermodynamics. Equating the terms to zero and simplifying gives,

$$\bar{v}dP - v'd\Pi = 0.$$

$v'$, the molecular volume in the ideal solution, is equal to $\frac{RT}{\Pi}$. Substituting this value in the last equation gives,

$$\frac{d\ln \Pi}{dP} = \frac{\bar{v}}{RT}.$$

The activity of $X_1$, $\xi$, is the same in the mixture A and the solution B and its value in terms of $\Pi$ is given by equation III. Substituting for $\Pi$ and expressing in the equation the constancy of temperature and composition,[9] we have,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_{T,N} = \frac{\bar{v}}{RT}. \qquad \text{(IX)}$$

This is the general equation for the influence of pressure upon the activity of one constituent of a binary mixture. The quantity $\bar{v}$ is of very great importance in the thermodynamics of mixtures. It is the increase in volume of an infinite quantity of a mixture when one mol of the constituent in question is added to it. We will call $\bar{v}$ the *partial molecular volume* of that constituent.

Similarly we may define the partial molecular energy, entropy, etc., and these quantities play the same rôle in the thermodynamics of mixtures that the molecular volume, energy, entropy, etc., do in the treatment of pure substances.

An important difference between the partial molecular volume in a mixture and the molecular volume of a pure substance is that while the latter is always positive the former need not be. Therefore the activity of one of the constituents of a mixture may either be increased or diminished by increase of pressure on the mixture.

[9] We will use the subscript $N$ with the partial differential coefficient to denote constancy of composition in the mixture.

If a mixture contains $X_1$ and $X_2$ in the proportion of $N_1$ mols of the former to $N_2$ of the latter, the relation of the partial molecular volumes, $\bar{v}_1$ and $\bar{v}_2$ is readily seen. If we add to an infinite quantity of the mixture $N_1$ mols of $X_1$, the mixture will increase in volume by $N_1\bar{v}_1$. Then adding $N_2$ mols of $X_2$ the volume increases by $N_2\bar{v}_2$. Altogether we have done nothing more than add one mol more of the original mixture. The total change of volume must therefore equal $v$, the volume of one mol of the mixture. Hence,

$$N_1\bar{v}_1 + N_2\bar{v}_2 = v. \qquad \text{X}$$

From equation IX we have the following two equations for the two constituents:

$$\left(\frac{N_1\partial \ln \xi_1}{\partial P}\right)_{T,N} = \frac{N_1\bar{v}_1}{RT},$$

$$\left(\frac{N_2\partial \ln \xi_2}{\partial P}\right)_{T,N} = \frac{N_2\bar{v}_2}{RT}$$

Adding these two, we obtain the important equation,

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2}{\partial P}\right)_{T,N} = \frac{v}{RT}.^{10} \qquad \text{XI}$$

The influence of temperature upon the activity of one of the constituents of a mixture may also be determined with the aid of the apparatus of Figure 1. Starting with the piston F at E, we may perform the following cycle of reversible operations, keeping the pressure constant upon both D and C.

(1) At the temperature $T$ raise the piston F until 1 mol of $X_1$ passes into B, where it occupies the volume $v'$. The pressure on F is kept at such a pressure, $\Pi$, that the activity of $X_1$ is always the same in B as in A.

(2) Lower the temperature to $T - dT$, moving the piston F so that none of $X_1$ passes through E. The volume of B is changed to $v' - dv'$ and the osmotic pressure to $\Pi - d\Pi$.

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[10] The equation is written in this form rather than in the more conventional form,

$$N_1\left(\frac{\partial \ln \xi_1}{\partial P}\right)_{T,N} + N_2\left(\frac{\partial \ln \xi_1}{\partial P}\right)_{T,N} = \frac{v}{RT},$$

in order to emphasize the peculiar significance of the term $N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2$. In general we shall see that the equations of a mixture may be obtained from those of a pure substance by substituting this series of terms in place of $\partial \ln \xi$.

(3) Lower F once more to E, under the constant pressure $\Pi - d\Pi$.
(4) Raise the temperature to T.

The total work done by the pistons D and C is zero, since they are under constant pressure and finally return to their original positions. The whole work done by the system is, therefore, the work done by the piston F. This is obviously the sum of the following four terms :

$$A_1 = \Pi v',$$
$$A_2 = -\Pi dv',$$
$$A_3 = -(\Pi - d\Pi)(v' - dv'),$$
$$A_4 = 0.$$

The sum of these terms, neglecting the differential of the second order, is $v'd\Pi$. This is the total work done by the system during the cycle, and therefore from the second law of thermodynamics,

$$v'd\Pi = \frac{Q}{T}dT,$$

where $Q$ is the heat absorbed in process (1). $Q$ is the sum of three terms. The first is the increase in internal energy when one mol of $X_1$ passes from A to B, which we may call $U_{(XII)}$. The second is the osmotic work, $\Pi v'$, which is equal to $RT$. The third is the work done by the pressure $P$ acting on piston D, which is equal to $-P\bar{v}$ where $\bar{v}$ is the partial molecular volume of $X_1$ as before.
Hence,

$$v'\frac{d\Pi}{dT} = \frac{U_{(XII)} + RT - P\bar{v}}{T}.$$

Now

$$v' = \frac{RT}{\Pi},$$

and therefore

$$\frac{d\ln\Pi}{dT} = \frac{U_{(XII)} + RT - P\bar{v}}{RT^2}.$$

Combining this equation with equations III and IV, as we did in deriving equation VIII, we have

$$\left(\frac{\partial\ln\xi}{\partial T}\right)_{P,N} = \frac{U_{(XII)} + U_{(IV)} - P\bar{v}}{RT^2}.$$

The sum of $U_{(XII)}$ and $U_{(IV)}$ is the increase in internal energy when one mol of $X_1$ passes from an infinite quantity of the mixture into a

state of infinitely attenuated vapor. We will denote this quantity by $\overline{\Upsilon}$. It bears the same relation to the value $\Upsilon$ of a pure substance as the quantity $\overline{v}$ does to $v$. We may call it the partial "ideal heat of evaporation."

The above equation then becomes,

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P,N} = \frac{\overline{\Upsilon} - P\overline{v}}{RT^2}, \qquad \text{XII}$$

which is a general equation for the influence of temperature upon the activity of one of the constituents of a mixture when the pressure and the composition are constant.[11]

Just as equation X was proved we may show that for one mol of the mixture,

$$\Upsilon = N_1\overline{\Upsilon}_1 + N_2\overline{\Upsilon}_2. \qquad \text{XIII}$$

Hence we obtain an equation analogous to equation XI, namely

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2}{\partial T}\right)_{P,N} = \frac{\Upsilon - Pv}{RT^2}. \qquad \text{XIV}$$

Here as before $v$ is the volume occupied by one mol of the mixture and $\Upsilon$ the increase in internal energy when one mol of the mixture is converted into infinitely attenuated vapor, or in other words when it evaporates in a vacuum.[12]

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[11] The approximate equation for the vapor pressure of one constituent of a binary mixture obtained from equation XII is,

$$\left(\frac{\partial \ln p}{\partial T}\right)_{P,N} = \frac{\overline{Q}}{RT^2},$$

where $\overline{Q}$ is the partial heat of vaporization (including the external work). This is in a simpler form than the equation obtained by Kirchhoff,

$$\left(\frac{\partial \ln \frac{p_0}{p}}{\partial T}\right)_{P,N} = \frac{\left(\frac{\partial Qx}{\partial x}\right)}{RT^2}$$

(see Nernst, Theoretische Chemie, 4 Edit., p. 118).

[12] Equation XII bears the same relation to XIV that the equation of Kirchhoff does to one obtained by Nernst, namely,

$$\frac{d \ln \frac{p_0}{p} + x d \ln \frac{p'_0}{p'}}{dT} = -\frac{Q(x)}{RT^2}$$

(Nernst Theor. Chem., 4 Edit, p. 117).

Finally we must determine how the activities of the components of a mixture vary when the composition is changed at constant temperature and pressure. In order to solve this problem we may employ the apparatus shown in Figure 2. A contains a mixture of $X_1$ and $X_2$. $E_1$ is a membrane permeable only to $X_1$, $E_2$ one permeable only to $X_2$. In $B_1$ and $B_2$ are ideal solutions of $X_1$ and $X_2$. The two pure ideal solvents lie above the pistons, $F_1$ and $F_2$, which are permeable only to these solvents. D is a piston which exerts a constant pressure on A. The pressure at $C_1$ and $C_2$ will also be held constant. We may perform the following isothermal cycle of reversible operations, starting with $N_1$ mols of $X_1$ and $N_2$ mols of $X_2$ in A, and none of these substances in $B_1$ and $B_2$, the pistons $F_1$ and $F_2$ being at $E_1$ and $E_2$.

(1) Keeping the pressures on $F_1$ and $F_2$ constant and at such values, $\Pi_1$ and $\Pi_2$, as to maintain equilibrium with the mixture in A, raise these two pistons at such rates that as $X_1$ and $X_2$ pass into $B_1$ and $B_2$ the remaining mixture in A still keeps its original composition. Finally, when all the mixture has disappeared from A there will be $N_1$ mols of $X_1$ in $B_1$ where it exerts the osmotic pressure $\Pi_1$, and occupies a volume which we will call $V_1$, and there will be $N_2$ mols of $X_2$ in $B_2$, the osmotic pressure being $\Pi_2$, and the volume $V_2$.

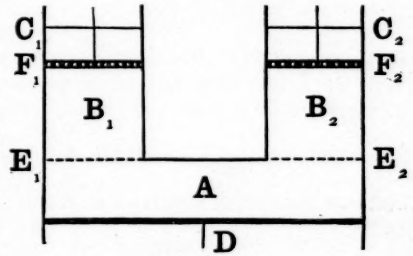

FIGURE 2.

(2) By simultaneous movements of the pistons $F_1$ and $F_2$ change the volumes in $B_1$ and $B_2$ to $V_1 - dV_1$ and $V_2 - dV_2$. The osmotic pressures will change to $\Pi_1 + d\Pi_1$ and $\Pi_2 + d\Pi_2$. The solutions in $B_1$ and $B_2$ are now able to exist in equilibrium, not with the original mixture, but with a mixture containing $X_1$ and $X_2$ in another proportion, say $N_1$ mols to $N_2 - dN_2$ mols.

(3) Form a mixture of this composition in A by lowering the pistons $F_1$ and $F_2$. This operation will be just the reverse of (1), except that $X_1$ and $X_2$ enter the mixture in the constant proportion, not of $N_1$ to $N_2$ but of $N_1$ to $N_2 - dN_2$. At the end of this process all of $X_1$ and all but $dN_2$ of $X_2$ will have passed into A.

(4) Finally force into A the remaining $dN_2$ mols of $X_2$, whereby the whole system returns to its original condition.

The work done during this cycle at D, $C_1$, and $C_2$, is zero, since in each case the final position is the same as the initial, and the pressure is constant throughout the cycle. Therefore the total work done by the system during the cycle is that done by the pistons $F_1$ and $F_2$, which is as follows:

In operation (1),

$$A_1 = \Pi_1 V_1 + \Pi_2 V_2.$$

In operation (2),

$$A_2 = -\Pi_1 dV_1 - \Pi_2 dV_2.$$

In operations (3) and (4), except for a differential of the second order,

$$A_3 + A_4 = -(\Pi_1 + d\Pi_1)(V_1 - dV_1) - (\Pi_2 + d\Pi_2)(V_2 - dV_2).$$

By the second law of thermodynamics the sum of these terms, the total work of a reversible isothermal process, must be zero. Hence, neglecting differentials of the second order,

$$V_1 d\Pi_1 + V_2 d\Pi_2 = 0.$$

Since we are dealing with ideal solutions,

$$V_1 = \frac{N_1 RT}{\Pi_1} \quad \text{and} \quad V_2 = \frac{N_2 RT}{\Pi_2},$$

hence

$$N_1 d \ln \Pi_1 + N_2 d \ln \Pi_2 = 0.$$

Now the activity $\xi_1$ of $X_1$ in A is always the same as in $B_1$, and $\xi_2$ in A is the same as in $B_2$; hence, applying equation III ($\rho$ and $T$ being constants) we have,

$$N_1 d \ln \xi_1 + N_2 d \ln \xi_2 = 0, \qquad \text{XV}$$

which may also be written

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial N_1}\right)_{P,T} = 0, \qquad \text{XV A}$$

or

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2}{\partial N_2}\right)_{P,T} = 0, \qquad \text{XV B}$$

It is not possible from thermodynamics alone to predict how the activity of each of the constituents of a binary mixture will change with a change in composition. But if the change in one of the activities is known, the change in the other may be found from the above simple relation.[13]

### Mixtures of More than Two Components.

In the derivation of equations IX and XII no use was made of the provision that the mixture contained but two constituents, and these equations therefore show the effect of pressure and of temperature upon the activity of one of the constituents of a mixture of any number of constituents. In the same way that equations XI, XIV, and XV were found we may obtain the following equations:

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2 + N_3\partial \ln \xi_3 + \cdots}{\partial P}\right)_{T,N} = \frac{v}{RT}, \qquad \text{XVI}$$

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2 + N_3\partial \ln \xi_3 + \cdots}{\partial T}\right)_{P,N} = \frac{\Upsilon - Pv}{RT^2}, \qquad \text{XVII}$$

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2 + N_3\partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{P,T} = 0. \qquad \text{XVIII}$$

### Dilute Solutions.

Equations XV and XVIII assume a very simple form when one of the constituents of a mixture is present in such small amount as to constitute a perfect solution. If a mixture consist of a very small amount of a substance $X_1$ and a large amount of a substance $X_2$, we may call the latter the solvent and the former the solute. If the solute is extremely dilute, then, according to equation II, its activity $\xi_1$ is proportional to its concentration and therefore to $N_1$. Hence,

$$d \ln \xi_1 = d \ln N_1,$$

and equation XV becomes,

$$N_2 d \ln \xi_2 = - dN_1, \qquad \text{XIX*}$$

or

$$d \ln \xi_2 = - \frac{dN_1}{N_2}. \qquad \text{XIX* A}$$

[13] An approximate equation which is a special form of equation XV is Duhem's equation for the vapor pressures of a binary mixture, namely, $N_1 d \ln p_1 + N_2 d \ln p_2 = 0$. This equation is true only when the vapors obey the gas law. See Lewis, Journ. Amer. Chem. Soc., **28**, 569 (1906).

This equation states that the relative lowering of the activity of a solvent by the addition of a small quantity of a solute is equal to the number of mols of solute divided by the number of mols of solvent.

This statement comprises in itself practically all the laws of dilute solutions. Raoult's law is a special but only approximate form of equation XIX, for equation XIX is true of every solution when infinitely dilute, but Raoult's law is not true even at infinite dilution, except when the vapor of the solvent is a perfect gas.

If the solute, $X_1$, is dissolved, not in a pure solvent, but in a mixture of $X_2$, $X_3$, etc., then for the perfect dilute solution we find in place of equation XIX,

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \cdots = - dN_1. \qquad XX^*$$

## Some Applications of the Preceding Equations.

Equations I–XX can be combined in a very great variety of ways to give important results. A few examples, however, will suffice to show the manner in which these equations may be employed.

First, as a simple example, we may derive the formula for the lowering of the freezing point of a perfect solution. According to equation XIX, the activity of a pure liquid is always lowered by the addition of a solute. If therefore a liquid and solid are together at the freezing point and a solute is added to the liquid, the activity of the latter will become lower than that of the solid, and the solid will melt. On the other hand, if we start again with liquid and solid at the freezing point and lower the temperature, we see from equation VIII that the activity of the solid will decrease faster than that of the liquid and the liquid will disappear. It is obvious, therefore, that by adding a solute to a freezing mixture and at the same time lowering the temperature by a suitable amount, the equilibrium between solid and liquid can be maintained. The necessary condition for the maintenance of equilibrium is that the activity $\xi_2$ of the solvent $X_2$ in the liquid state remain equal to the activity $\xi'_2$ of $X_2$ in the solid state. Hence,

$$d \ln \xi'_2 = d \ln \xi_2.$$

Now, assuming that the solid does not dissolve any of the solute, the change in activity of the solid $X_2$ is due merely to change of temperature, and thus from equation VIII,

$$d \ln \xi'_2 = \frac{Y'_2 - Pv'_2}{RT^2} dT.$$

But the activity of the solvent in the liquid phase is changed both by the change in temperature and by the presence of $dN_1$ mols of solute. That is,

$$d \ln \xi_2 = \left(\frac{\partial \ln \xi_2}{\partial T}\right) dT + \left(\frac{\partial \ln \xi_2}{\partial N_1}\right) dN_1.$$

Whence by means of equations XII and XIX

$$d \ln \xi_2 = \frac{\bar{Y}_2 - P\bar{v}_2}{RT^2} dT - \frac{dN_1}{N_2}.$$

Equating the second members of this equation and the one above,

$$\frac{Y'_2 - Pv'_2}{RT^2} dT = \frac{\bar{Y}_2 - P\bar{v}_2}{RT^2} dT - \frac{dN_1}{N_2},$$

or

$$-N_2 \frac{dT}{dN_1} = \frac{RT^2}{Y'_2 - Pv'_2 - \bar{Y}_2 + P\bar{v}_2}.$$

But it is obvious on inspection that the denominator of the second member is merely the heat of fusion of one mol of solid, which we may call $Q$. If the solution is very dilute we may also simplify by writing $N_2 = 1$. Hence,

$$\frac{dT}{dN_1} = -\frac{RT^2}{Q}.$$

This is the familiar equation of van't Hoff for the lowering of the freezing point by a dissolved substance.

As a second example we may study the following system. A mixture of $X_2$ and $X_3$ in the molecular proportion of $N_2$ to $N_3$ are in equilibrium with a second phase consisting of pure $X_2$. Let us determine the change in activity of $X_3$ when a small quantity $dN_1$ of a substance $X_1$ is dissolved in the mixture. At constant temperature and pressure the activity $\xi'_2$ of the pure phase of $X_2$ is a constant, and therefore the activity, $\xi_2$, of $X_2$ in the mixture is also constant. Equation XX therefore becomes,

$$N_3 d \ln \xi_3 = -dN_1. \qquad \text{XXI}$$

This interesting equation has, I believe, not hitherto been obtained, even in an approximate form. Its meaning may be illustrated by the following example: If a saturated solution of salt in 1000 grams of water is in contact with solid salt, and 1 gram of sugar is added, then

the activity of the water is lowered by the same per cent as when 1 gram of sugar is added to 1000 grams of pure water.

An interesting system is one composed of two phases, both of which are mixtures of the same composition. An important example of such a system is a constant boiling mixture and its saturated vapor. Here $N_2$, $N_3$, etc., which are the molecular fractions in the one phase, are equal respectively to $N'_2$, $N'_3$, etc., in the other phase. If the conditions are changed by changing the temperature or pressure or by adding a third substance $X_1$ to one or both of the phases, then equilibrium can only be maintained by keeping the activity of each component the same in both phases; thus we may write as usual,

$$d \ln \xi_2 = d \ln \xi'_2, \qquad d \ln \xi_3 = d \ln \xi'_3,$$

etc.; but since $N_2 = N'_2$, etc., we may write

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \cdots = N'_2 d \ln \xi'_2 + N'_3 d \ln \xi'_3 + \cdots$$

Now the first member of this equation represents a change which may be the resultant of the changes produced by change of temperature, change of pressure, and the addition of $dN_1$ mols of the solute $X_1$. Each of these changes is represented alone by equations XVI, XVII, or XX. Therefore,

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial T}\right)_{P,N} dT = \frac{\Upsilon - Pv}{RT^2} dT,$$

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial P}\right)_{T,N} dP = \frac{v}{RT} dP,$$

$$\left(\frac{N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{T,P} dN_1 = - dN_1.$$

We may therefore write the sum of these as follows:

$$N_2 d \ln \xi_2 + N_3 d \ln \xi_3 + \cdots = \frac{\Upsilon - Pv}{RT^2} dT + \frac{v}{RT} dP - dN_1.$$

Likewise we find

$$N'_2 d \ln \xi'_2 + N'_3 d \ln \xi'_3 + \cdots = \frac{\Upsilon' - Pv'}{RT^2} dT + \frac{v'}{RT} dP - dN'_1,$$

where $dN'_1$ is the number of mols of the solute in one mol of the second phase. Equating the second members of these two equations we have,

$$\frac{(\Upsilon - Pv) - (\Upsilon' - Pv')}{RT^2}\,dT + \frac{(v - v')}{RT}\,dP - dN_1 + dN'_1 = 0.$$

The numerator of the first term, which we may call $Q$, is obviously the heat absorbed when a mol of the mixture passes from the first phase to the second, and $(v - v')$ is the decrease in volume accompanying the same change. Thus,

$$\frac{Q}{RT^2}\,dT + \frac{v - v'}{RT}\,dP - dN_1 + dN'_1 = 0. \qquad \text{XXII*}$$

This extremely general equation shows how the variations in temperature, pressure, and quantity of solute must be regulated in order to maintain equilibrium in such a system. Several special cases are worthy of notice. If pressure and temperature are the only variables, in other words if $dN_1$ and $dN'_1$ are zero, then the equation becomes,

$$\frac{dP}{dT} = \frac{Q}{(v' - v)\,T}.$$

This equation is identical with the familiar Clapeyron-Clausius equation. It shows, for example, that the vapor pressure from a constant boiling mixture varies with the temperature in the same way that the vapor pressure of a pure substance does.

If in equation XXII, $dP$ and $dN'_1$ are zero, there remains an equation for the change in temperature which compensates for the addition of a solute soluble in one phase only, namely,

$$dT = \frac{RT^2}{Q}\,dN_1.$$

Thus, for example, the boiling point of a constant boiling mixture is changed by the addition of a non-volatile solute according to the same law as that which applies in the case of a simple solvent.[14] $Q$ is of course the heat of vaporization of one mol of the mixture.

In the same way, by making $dT$ equal to zero in equation XXII, a formula may be derived for the lowering of the vapor pressure of a constant boiling mixture when a solute is added at constant temperature.

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[14] This equation I have already proved in a less rigorous way (Journ. Amer. Chem. Soc., **28**, 766, 1906). It has considerable practical importance, as it increases the number of solvents in which molecular weights may be determined by the boiling point method.

If instead of the system considered above we study a system of the type represented by a mixture at its eutectic point, we may derive a set of equations, entirely similar to the above, which show the change of the eutectic temperature with the pressure, and the change of the eutectic temperature at constant pressure, or of the eutectic pressure at constant temperature, when a solute is added to the mixture.

These examples will suffice to show the way in which equations I–XX may be applied to the derivation of other thermodynamic equations.

## The Laws of Chemical Equilibrium.

Hitherto we have considered only those processes in which each molecular species persists without any change except that of passing from one phase to another. We will now consider those processes in which the molecular species react with each other to form new species, and it will be shown that the activity of a given species is not only a measure of the tendency of that species to escape into some other phase, but is also a perfect measure of the tendency of the species to take part in any chemical reaction. In other words, the activity is an exact measure of that which has been rather vaguely called the "active mass" of a substance.

Let us consider the reaction represented by the following equation,

$$aA + bB + \cdots \leftrightarrows oO + pP + \cdots,$$

where $a$ mols of the substance A, $b$ mols of B, etc., combine to form $o$ mols of O, $p$ mols of P, etc. The several substances may exist in the pure state, or in mixtures; may be in one phase or in different phases, and there may be other substances present which take no part in the reaction. In other words, we are considering any system whatever in which a given chemical reaction occurs. Let us find the conditions for equilibrium in this reaction.

We may choose a liquid which is an ideal solvent for each of the substances taking part in the reaction. If this ideal solvent is brought in contact with the system through a membrane permeable only to the substances which take part in the reaction, these substances will enter the solvent, and when the system comes to a final condition there will be equilibrium in the chemical reaction, both in the original system and in the ideal solution. Moreover, the activity of each of the molecular species must be the same throughout the original mixture and in the ideal solution.

Now in the ideal solution it is easy to show rigorously, as van't Hoff has done, that the condition of equilibrium at a given temperature is,

$$\frac{C_O^o C_P^p \cdots}{C_A^a C_B^b \cdots} = \text{constant.}$$

where $C_A$, etc., represent the concentrations. But in this solution the concentrations are proportional to the activities, and therefore,

$$\frac{\xi_O^o \xi_P^p \cdots}{\xi_A^a \xi_B^b \cdots} = K. \qquad \text{XXIII}$$

where $K$ is another constant. Since the activities $\xi_A$, etc., are not only the activities in the ideal solution, but also in the original system, it is obvious that equation XXIII expresses a law of extraordinary generality.

The above quotient, which we have called $K$, has a value which, for a given reaction at a given temperature, does not depend upon the medium in which the reaction occurs, nor upon the concentrations, nor upon the pressure, nor upon the nature or number of the phases which are concerned in the reaction. In other words $K$ depends only upon the temperature and the specific nature of the reaction. It is therefore a better measure of the true "affinity" of a chemical reaction than any quantity that has hitherto been used for this purpose.

The equilibrium ratio, $K$, changes with the temperature according to a simple law. We may imagine the substances taking part in a given reaction all vaporized in a space so large that each vapor behaves like a perfect gas. If the reaction reaches equilibrium under these conditions, it is easy to show that the following equation of van't Hoff is entirely exact, namely,

$$\frac{d \ln \frac{C_O^o C_P^p \cdots}{C_A^a C_B^b \cdots}}{dT} = \frac{\mathfrak{U}}{RT^2},$$

where $C_A$, $C_B$, etc., represented the concentrations, and $\mathfrak{U}$ is the increase in internal energy when the reaction occurs in this extremely attenuated gaseous phase.

Since we are dealing with infinitely attenuated vapors, $C_A$, etc., may be replaced by $\xi_A$, etc., whence

$$\frac{d \ln K}{dT} = \frac{\mathfrak{U}}{RT^2}. \qquad \text{XXIV}$$

Since at constant temperature $K$ is independent of the conditions under which a reaction occurs, it is obvious that the change with the temperature of the equilibrium ratio of the reaction in any system whatever is given in equation XXIV. The important quantity U, the heat of reaction in the dilute gaseous phase, is equal to the heat of reaction in any other condition less the algebraic sum, for all the substances taking part in the reaction, of the quantities which we have denoted by the symbol Y.

The importance of this quantity U has been recognized by Berthelot, who wrote in 1875,[15] "J'ai défini spécialement *la chaleur de combinaison atomique*, laquelle exprime le travail réel des forces chimique, et doit être rapportée à *la réaction des gaz parfaits, opérée à volume constant.*"

The following interesting example will serve to illustrate the simultaneous application of equation XXIII or XXIV with the preceding equations. Let us prove the theorem first demonstrated by Stortenbeker,[16] namely, that the freezing point of a substance like $CaCl_2 \cdot 6H_2O$ which partly dissociates in the liquid phase, is not changed by the addition to the liquid of a small quantity of either of the products of dissociation ($CaCl_2$ or $H_2O$). When the solid, $CaCl_2 \cdot 6H_2O$, melts, there are in the liquid $N_1$ mols of $CaCl_2 \cdot 6H_2O$, to $N_2$ mols of $CaCl_2$ and $N_3$ mols of $H_2O$, where $N_3 = 6N_2$. Let us find the effect produced by adding $dN_3$ mols of $H_2O$ at constant temperature and pressure. According to equation XVIII,

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + N_3 \partial \ln \xi_3}{\partial N_3}\right)_{P,T} = 0.$$

From this equation, since $N_3 = 6\ N_2$, it is obvious that,

$$N_1 d \ln \xi_1 + N_2 (d \ln \xi_2 + 6\, d \ln \xi_3) = 0.$$

Now since the $CaCl_2 \cdot 6H_2O$, $CaCl_2$, and $H_2O$ are in equilibrium, equation XXIII states that,

$$\frac{\xi_2 \xi_3^6}{\xi_1} = K.$$

Taking the logarithm of both members and differentiating we have,

$$d \ln \xi_2 + 6\, d \ln \xi_3 = d \ln \xi_1.$$

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[15] Ann. Chim. Phys., **4**, 1 (1875).

[16] Zeit. phys. Chem., **10**, 183 (1802).

Combining this equation with the above gives,

$$N_1 d\ln\xi_1 + N_2 d\ln\xi_1 = 0, \quad \text{or} \quad d\ln\xi_1 = 0.$$

That is, the activity of the $CaCl_2 \cdot 6\ H_2O$ in the liquid phase is not changed by the addition of a small quantity of water, and it will therefore remain in equilibrium with the solid $CaCl_2 \cdot 6\ H_2O$ without change in the freezing point.

This example illustrates the general manner of treatment of systems in which molecular species may change through dissociation, association, or through the mutual reaction of two or more species.

A little consideration of the simultaneous use of equations XXIII and XXIV with the preceding equations shows why it is that such equations as V and VIII hold for the activity of a molecular species such as $H_2O$, in a given pure phase, regardless of whether this phase is really composed entirely of the species $H_2O$ or in part also of others such as $(H_2O)_2$, $(H_2O)_3$, $(H^+ + OH^-)$, etc., provided always that these other species can be formed from, and are in equilibrium with, the molecular species $H_2O$.

It may seem, at first sight, that equations XXIII and XXIV, as well as the preceding equations, while entirely exact and general in their scope, may not be readily applied to certain concrete problems where the value of the activity cannot be obtained from existing data. As a matter of fact, however, it is seldom important to know the numerical value of the activity in any one state, but rather the ratio between the activity of a substance in one state and that in another, and this ratio may be obtained in a variety of ways.

In fact one of the most important problems to which the equations derived in this paper may be applied, concerns the dissociation of salts in aqueous solutions into their ions, although from the nature of the ions we are never able to determine the numerical values of their activities. Let us consider the dissociation of such a substance as hydrochloric acid in aqueous solution, according to the reaction,

$$HCl = H^+ + Cl^-.$$

According to the ordinary mass law,

$$\frac{C_H C_{Cl}}{C_{HCl}} = K.$$

Now this equation has been shown to be false, if we calculate the concentration of the ions from conductivity data. In all probability

this calculation is correct for solutions more dilute than tenth normal,[17] at least we may say that *the conductivity data furnish the only means we have at present for calculating the ion concentrations. Every other method which has been employed measures not the concentrations, but the activities of the ions.*

According to equation XXIII the activities of the undissociated acid and the ions are connected by the equation,

$$\frac{\xi_H \xi_{Cl}}{\xi_{HCl}} = K.$$

If therefore the mass law is false, it must be because the activity is not simply proportional to the concentration for one or more of these three substances. The problem, therefore, is to determine how the activity of the undissociated substance and the activity of the ions vary with the concentrations of both. It seems that all the facts which are at present known concerning electrolytic dissociation can be explained by the assumption that the ions are normal in their behavior; in other words, that the activity of each ion is simply proportional to its concentration, but that the undissociated portion of a strong electrolyte is abnormal in its behavior, the activity being proportional to the concentration of the undissociated substance multiplied by a quantity which depends solely on the total ion concentration, and increases with the latter.[18]

This simple statement suffices to explain qualitatively all the known anomalies of strong electrolytes. The exact quantitative formulation of this principle can hardly be made until still more experimental work has been done.

However, these considerations illustrate the method of treating chemical equilibrium when the ordinary mass law fails; in other words, when for one or more of the reacting substances the activity is not proportional to its concentration. For a complete analysis of such a case it is necessary to know how the activity of each of the reacting substances changes with its concentration and with the concentration of the other substances present.

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[17] The data upon which this paragraph is based are chiefly those contained in the very complete and instructive summary by A. A. Noyes, entitled, "The Physical Properties of Aqueous Salt Solutions in Relation to the Ionic Theory." (Technology Quarterly, **17**, 293, 1904).

[18] Probably, strictly speaking, the activity of the ions is likewise a function of the concentration of the undissociated substance, decreasing as the latter increases; but since the concentration of the undissociated substance always is very small in dilute solutions of strong electrolytes, its influence on the activity of the ions is therefore of minor importance.

## The Relation of Activity to Free Energy and Thermodynamic Potential.

It is interesting to see what relation the activity bears to certain other quantities which have been previously used for a similar purpose, especially the free energy of Helmholtz, which is itself intimately related to the various thermodynamic potentials.

The diminution in free energy which accompanies a given isothermal process, that is, the maximum work which the process may accomplish, is not a definite quantity until we define not only the process but also the system which is to be considered. To illustrate, we may consider a cylinder containing liquid and vapor, and a piston operated on by a spring which exerts a force exactly balancing the vapor pressure. When the piston moves out an infinitesimal distance, the decrease in free energy of the water and vapor is equal to $pdV$, but on the other hand the free energy of the spring increases by $pdV$, so that the free energy of the system comprising water, vapor, and spring does not change. In general we shall depart from the most common usage and consider the larger system, and we may therefore define the diminution in free energy of a given isothermal process as the maximum work which the process is able to accomplish, exclusive of the work done against the external pressure or pressures. The negative of this quantity, the increase in free energy, we shall denote by $\Delta\mathfrak{F}$.[19] In a system whose properties are determined when the temperature, the pressure, and the compositions of the various phases are fixed, the general condition of equilibrium is that,

$$\delta\mathfrak{F} = 0.$$

Let us now consider the change in free energy when one mol of a given molecular species passes from one state where its activity is $\xi$, to another state where its activity is $\xi'$. This change may be effected as follows: (1) Pass one mol reversibly from the first state into an ideal solvent. The solution will have the osmotic pressure $\Pi$ and the volume $v$. (2) Change the concentration reversibly until the volume becomes $v'$ and the osmotic pressure reaches such a value, $\Pi'$, that the

[19] The completely general definition of free energy is given by the equation,

$$-\Delta\mathfrak{F} = W_{max} + P_1V_1 + P'_1V'_1 + \cdots - P_2V_2 - P'_2V'_2 - \cdots$$

$W_{max}$ is the total work obtainable in the process in which system I, comprising one portion of volume $V$, at pressure $P_1$, another of volume $V_2$, at pressure $P_2$, etc., passes over into system II, comprising one portion of volume $V_2$, at pressure $P_2$, another of volume $V'_2$, at pressure $P'_2$, etc. The free energy as thus defined is identical with the thermodynamic potential, $\zeta$, of Gibbs.

solution is now in equilibrium with the substance in the second state. (3) Let the substance pass reversibly out of the ideal solution into the second state. In the first step $\Delta_1 \mathfrak{F} = - \Pi v$. In the second, $\Delta_2 \mathfrak{F} = RT \ln \frac{\Pi'}{\Pi}$. In the third, $\Delta_3 \mathfrak{F} = \Pi' v'$. Since by equation III the activities are proportional to the osmotic pressures in the ideal solution, and since $\Pi v = \Pi' v'$, the total increase in free energy is,

$$\Delta \mathfrak{F} = RT \ln \frac{\xi'}{\xi}. \qquad \text{XXV}$$

This is a general equation for the change in free energy in the passage of one mol of a given species from one state to another when the species itself does not change.[20] When we are dealing with the most general case of chemical reaction, when $a$ mols of A, $b$ mols of B, etc., combine to form $o$ mols of O, $p$ mols of P, etc., the total change in free energy will obviously be equal to that which accompanies the transfer of the factors of the reaction from the original system to another system where there is equilibrium, and the transfer of the products from this equilibrium system to the original system. By a combination, therefore, of equations XXIII and XXV, we find,

$$\Delta \mathfrak{F} = RT \ln \frac{\xi_O^o \xi_P^p \cdots}{\xi_A^a \xi_B^b \cdots} - RT \ln K. \qquad \text{XXVI}$$

Here $\Delta \mathfrak{F}$ is the increase in free energy in any reaction when $\xi_A$, $\xi_B$, etc., are the activities of the factors, $\xi_O$, $\xi_P$, etc., those of the products, and $K$ is the equilibrium ratio.

## Electromotive Force Equations.

The change of free energy of a reversible galvanic cell is a direct measure of the electrical work of the cell. If $E$ is the electromotive force of the cell, and $F$ is the Faraday equivalent, then,

$$\Delta \mathfrak{F} = - mFE,$$

where $m$ is the number of Faraday equivalents which pass through the cell during the reaction in question, and in the direction in which the electromotive force $E$ tends to send the current.

[20] It would have been possible at the beginning to define the activity by means of this equation, and this would have led to a development of our set of equations, which from a mathematical standpoint would have been simpler than the one here adopted.

This value of $\Delta\mathfrak{F}$ may now be substituted in equations XXV and XXVI. The former gives a formula for the electromotive force when only one substance takes part in the electrolytic process, as in certain concentration cells. The latter gives a general equation for any reversible cell whatever. These are,

$$E = \frac{RT}{mF} \ln \frac{\xi}{\xi'}, \qquad \text{XXVII}$$

$$E = \frac{RT}{mF} \ln K - \frac{RT}{mF} \ln \frac{\xi_O^o \xi_P^p}{\xi_A^a \xi_B^b}. \qquad \text{XXVIII}$$

In XXVII, $m$ is the number of Faraday equivalents accompanying the passage of one mol; in XXVIII, it is the number accompanying the disappearance of $a$ mols of A, $b$ mols of B, etc.

One application of equation XXVII is of special interest. We may take it for granted that whenever two phases are in contact and a given molecular species is present in one of them, it will be present to some extent in the other. For example, if a rod of metallic silver dips into a solution of silver nitrate, we may suppose that silver ions are present not only in the solution, but also in the metal. The process which takes place at this electrode during the passage of a current may therefore be regarded as consisting in the passage of silver ions out of the electrode into the solution, or vice versa. Equation XXVII gives us, therefore, an expression for the *single potential difference* between an electrode and an electrolyte. If the ion in question is an elementary one (and monatomic) $m$ is equal to $\nu$, the valence of the ion, and we may write equation XXVII in the following form,

$$E = \frac{RT}{\nu F} \ln \frac{\xi_M}{\xi_S} \qquad \text{XXIX}$$

where $E$ is the single potential difference, $\xi_M$ is the activity of the ion in question in the electrode, and $\xi_S$ is the activity of the same ion in the electrolyte. It is obvious that the quantity $\xi_M$ is very similar to the electrolytic solution pressure of Nernst, but while the latter depends at a given temperature, not only upon the character of the electrode but also upon the nature of the medium in which the electrolyte is dissolved, $\xi_M$ depends solely upon the character of the electrode. Moreover, while equation XXIX is universally true, the equation of Nernst is obviously only true when the activity of the ion in the electrolyte is proportional to its concentration. We have in the application of equations XXIX (or XXVII) to the electromotive

force of concentration cells a remarkably useful means of determining, in the case of imperfect solutions, how the activity of a given molecular species varies with the concentration.

## Summary.

It has been shown that a quantity named the activity, and closely related to the fugacity of the preceding paper, may be so defined that it serves as an ideal measure of the tendency of a given molecular species to escape from the condition in which it is. With the aid of this quantity a series of equations has been obtained, which have the same form as the approximate equations now in common use, but which are perfectly exact and general. The utility of these equations has been illustrated by their application to a number of special problems. From each equation two approximate equations can be immediately obtained, one for the vapor pressure of a substance, the other for its solubility. From equations XXIII, and following, important approximate equations are obtained by substituting concentrations for activities. The most general of the equations are collected for reference in the following list:

For a pure substance,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_T = \frac{v}{RT}, \qquad \text{V}$$

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_P = \frac{\Upsilon - Pv}{RT^2}. \qquad \text{VIII}$$

For one constituent of a mixture,

$$\left(\frac{\partial \ln \xi}{\partial P}\right)_{T,N} = \frac{\bar{v}}{RT}, \qquad \text{IX}$$

$$\left(\frac{\partial \ln \xi}{\partial T}\right)_{P,N} = \frac{\bar{\Upsilon} - P\bar{v}}{RT^2}. \qquad \text{XII}$$

For all the constituents of a mixture,

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + \cdots}{\partial P}\right)_{T,N} = \frac{v}{RT}, \qquad \text{XVI}$$

$$\left(\frac{N_1 \partial \ln \xi_1 + N_2 \partial \ln \xi_2 + \cdots}{\partial T}\right)_{P,N} = \frac{\Upsilon - Pv}{RT^2}, \qquad \text{XVII}$$

$$\left(\frac{N_1\partial \ln \xi_1 + N_2\partial \ln \xi_2 + \cdots}{\partial N_1}\right)_{P,\,T} = 0. \qquad \text{XVIII}$$

For a perfect dilute solution,

$$\left(\frac{N_2\partial \ln \xi_2 + N_3\partial \ln \xi_3 + \cdots}{\partial N_1}\right)_{P,\,T} = -1. \qquad \text{XX*}$$

For the most general case of chemical equilibrium at a given temperature,

$$\frac{\xi_O^o \xi_P^p \cdots}{\xi_A^a \xi_B^b \cdots} = K \text{ (a constant).} \qquad \text{XXIII}$$

For the change in the equilibrium ratio of any reaction with the temperature,

$$\frac{d \ln K}{dT} = \frac{\mathfrak{U}}{RT^2}. \qquad \text{XXIV}$$

For the increase in free energy when one mol of a given substance passes from one state to another,

$$\Delta\bar{\mathfrak{F}} = RT \ln \frac{\xi'}{\xi}. \qquad \text{XXV}$$

For the increase in free energy in any chemical reaction,

$$\Delta\bar{\mathfrak{F}} = RT \ln \frac{\xi_O^o \xi_P^p \cdots}{\xi_A^a \xi_B^b \cdots} - RT \ln K. \qquad \text{XXVI}$$

For the electromotive force of any reversible cell,

$$E = \frac{RT}{m\mathfrak{F}} \ln K - \frac{RT}{m\mathfrak{F}} \ln \frac{\xi_O^o \xi_P^p \cdots}{\xi_A^a \xi_B^b \cdots}. \qquad \text{XXVIII}$$

For the single potential at any electrode,

$$E = \frac{RT}{\nu\mathfrak{F}} \ln \frac{\xi_M}{\xi_S}. \qquad \text{XXIX}$$